REPORT DOCUMENTATION

AD-A255 979

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	31 Aug 92	FINAL 01 NOV 88 through 31 OCT 91

4. TITLE AND SUBTITLE
Final Technical Report 1989-1991 AFOSR-89-0132

5. FUNDING NUMBERS
~~G-AFOSR-88-0132~~
61102F
2303/B3

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8. PERFORMING ORGANIZATION REPORT NUMBER
AFOSR-TR- 92 0965

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Air Force Office of Scientific Research
Department of the Air Force
Bolling Air Force Base, DC 20332-6448
NC

10. SPONSORING/MONITORING AGENCY REPORT NUMBER
AFOSR 89-0132

11. SUPPLEMENTARY NOTES

DTIC ELECTE S OCT 1 1992 C D

12a. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release;
distribution unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

We have achieved two objectives: (1) we developed the theory of electron scattering by adsorbed molecule and used it to demonstrate that electron scattering is a good probe of the orientation of a chemisorbed molecule. (2) We developed the theory of photodissociation with ultrashort pulses, analyzed existing experiments and showed that coherence and interference play a central role in the dissociation process. By using numerical simulations we proposed and documented new types of experiments which can increase the amount of information regarding dynamics of dissociation.

92 10 6 082

07425

92-26601 13 pgs

14. SUBJECT TERMS	15. NUMBER OF PAGES	16. PRICE CODE
	10	

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
Unclassified	Unclassified	Unclassified	UL

Final Technical Report 1989-1991

AFOSR-89-0132

(a) List of objectives: We have pursued two objectives. (1) We have established that one can use electron scattering to determine the structure of molecules adsorbed on metal surfaces. (2) We have developed theoretical methods for the analysis of photo-dissociation experiments performed with femtosecond pulses.

(b) Status of the research effort: We have developed a computer code that allows us to calculate accurately the differential cross sections for electron scattering by adsorbed molecules. The program has a number of very useful features: it can use Hartree - Fock or configuration interaction wave functions to describe the electron scattering resulting in the electronic excitation of an excited molecule; if can be applied to molecules of reasonable size and has no restrictions regarding the molecular symmetry.

We have calculated the dependence of the differential cross section on the energy of incidence, angle of incidence, angles of detection and molecular orientation for several molecules. For H_2 we calculated the cross section for scattering causing electronic excitations (ref. 134). For H_2O, CO and N_2 we have calculated elastic scattering cross sections (refs. 139, 144). Vibrational inelastic scattering has been calculated for CO.

These calculations have established that the differential cross section for electron scattering is very sensitive to the orientation of the adsorbate with respect to the surface and can be used to determine it.

We have also written an article regarding the symmetry rules (ref. 168)

governing electron scattering by adsorbates, which allows us to establish simple qualitative connections between adsorption geometry and the angular pattern of the scattered electrons.

We have also pursued theoretical studies of photochemistry with femtosecond pulses. Some of the work was motivated by Zewail's experiments which are funded by the AFOSR.

In our work we obtain exact solutions for the time dependent Schrödinger equation for models that either mimic closely the laboratory conditions, or provide a reasonable representation of the behavior of a "typical" molecule. I regard our studies as computer experiments, because our conclusions are as reliable as the time dependent Schrödinger equation.

Our research has evolved in several directions that complement each other: (α) the improvement of the existing computational methods and the development of new ones; (β) the development of the time dependent formulation of cw spectroscopy with applications to photodissociation; (χ) theoretical studies of existing femto second pump - probe experiments; (δ) the development and the illustration of new concepts in short pulse photochemistry; (ε) exploratory studies of experiments on new systems.

The computer power needed in our work is at the upper range of what is currently available. Because of this we are forced to give numerical methodology more attention than we would like. We solve the time dependent Schrödinger equation by using fast Fourier transform methods. In the past we have extended this method to systems with curve crossing and introduced a procedure for dealing efficiently with slow dissociation.

Within the fast Fourier transform codes bending and rotational motion are treated through standard eigenfunction expansions. This increases dramatically the computer time and makes programming very tedious. Recently we have managed to develop a fast Fourier method directly applicable to angular variables (ref. 181), which is an order of magnitude faster, is a lot easier to implement and does not requires changing the program every time one deals with a new molecule. We can now calculate with relative ease, the photodissociation dynamics of triatomic molecules caused by one or two photon processes. The great advantage of this method is that it provides an intuitive description of the dissociation dynamics in time and space as opposed to an abstract superposition of eigenstates. We plan to continue this line of work until we have efficient methods for all problems involving triatomics: reactive collisions, spectroscopy and photodissociation.

A while ago we have started to develop the methodology necessary for interpreting cw spectra of photodissociating molecules in terms of the nuclear dynamics on the upper potential energy surface. This line of work put some computational muscle behind Heller's earlier ideas, turning them into practical tools to interpret spectra and adding some new concepts. The only AFOSR supported paper in this series is ref. 173. There we show that the predissociation line shape provides detailed information regarding the dynamics of predissociation on a femto second time scale. We have also shown how one can do femto second studies of photodissociation by performing low resolution absorption spectroscopy. Recently we started new applications of this technique: we are calculating the spectrum of a sodium doped zeolite. This shows that the sodium

atom loses an electron which becomes delocalized over eight Si atoms of the zeolite framework. The adsorption spectrum of this electron is very sensitive to the amount of charge on the Si atom. This is very poorly known and we can determine the the Si charge by comparing the calculated spectra with measurements in progress at Santa Barbara.

(χ) Theoretical studies of pump-probe experiments with femtosecond pulses: Zewail's experiments (sponsored by AFOSR) have been a constant source of inspiration for us and we have already examined theoretically his NaI (refs. 159, 166, 171), ICN (ref. 170) and I_2 (ref. 183) measurements. These timely, high quality studies have contributed much to our current understanding of real time photodissociation experiments, explaining the quantum mechanics behind the experimental observations. Without false modesty, we have provided the most thorough analysis of these phenomena so far.

(δ) New concepts: Computer experiments allow us to explore new concepts and to suggest new laboratory experiments. We have used this capability to study the role that the excitation transients, the coherence of the wave function and quantum interference might play in short pulse photodissociation. We have shown that energy resolved detection (which is, unfortunately, more easily performed on a computer than in the laboratory) could enhance enormously the amount of information provided by pump and probe spectroscopy. The main point is that the combined effect of short pulse excitation and photodissociation is to prepare the products in a coherent state which, if appropriately probed, leads to beats in the signal. These beats are state specific and their onset and evolution depends intimately on the manner in which the photodissociation dynamics builds up the final state distribution. We have demonstrated existence of such

beats for the rotational distribution (ref. 170), the final state vibrational distribution (ref. 170) and the vibrations of the transition complex formed during predissociation (ref. 178).

The excitation with short pulses creates transient wave functions which cannot be observed in cw experiments. We have shown that the vibrational distribution of the products during predissociation builds slowly, after excitation by a short pump pulse, and it looks dramatically different at different delay times (ref. 174). Furthermore, the transient states created by the cw excitation of the molecule at frequencies at which the absorption cross section is zero can be detected by using ultrashort pulses.

Finally, we have also studied the possibility of using one photon multiple pulse experiments (ref. 175) to display quantum interference during photodissociation. We have shown that by using two identical pulses we can enhance the photodissociation yield by more than a factor of two or we can use one pulse to substantially erase the effect of a previous pulse.

(c) Publications sponsored by AFOSR-89-0132:

134. On the Possibility of Using Differential Cross Section Measurements For the Electronic Excitation of Adsorbates By an Electron Beam, to Determine the Adsorbate Orientation, S. Nagano, Z.-P. Luo, H. Metiu, W.H. Huo, M.A.P. Lima, V. McKoy, J. Chem. Phys. 85, 6153 (1986).

139. The Connection Between the Orientation of Adsorbed Water and the Differential Cross Section of Elastic Electron Scattering, S. Nagano, Z-P. Luo, H. Metiu, W. Huo, M. Lima and V. McKoy, Surf. Sci. Lett. 186, 548 (1987).

144. Electron Scattering Distributions As a Probe of Adsorbate Orientation: CO and N_2, S. Nagano, Z-P. Luo, H. Metiu, W.M. Huo and V. McKoy, J. Chem. Phys. 88, 7970 (1988).

159. Molecular State Evolution After Excitation with an Ultra-Short Laser Pulse: An Exact Quantum Analysis of NaI and NaBr Dissociation, V. Engel, H. Metiu, R. Almeida, R.A. Marcus and A.H. Zewail, Chem. Phys. Lett. 152, 1 (1988).

166. A Quantum Mechanical Study of Predissociation Dynamics of NaI Excited by a Femtosecond Laser Pulse, V. Engel and H. Metiu, J. Chem. Phys. 90, 6116 (1989).

168. Determination of Adsorbate Orientation from Symmetry Rules in Low-Energy Elastic Electron Scattering, C. Winstead, V. McKoy and H. Metiu, Surface Sci. 217, L442 (1989).

169. Determination of Adsorbate Orientation from Symmetry Rules in Low-Energy Elastic Electron Scattering, C. Winstead, V. McKoy and H. Metiu, Surface Sci. 217, L442 (1989).

170. Rotational Coherence Effects in Femtosecond Pump-Probe Studies of Triatomic Photodissociation: Application to ICN, R. Heather and H. Metiu, Chem. Phys. Lett. 157, 505 (1989).

171. Two Photon Excitation of NaI with Femtosecond Laser Pulses, V. Engel and H. Metiu, J. Chem. Phys. 91, 1596 (1989).

173. A Time Dependent Interpretation of the Absorption Spectrum of CH_3ONO, V. Engel, R. Schinke, S. Hennig and H. Metiu, J. Chem. Phys., 92, 1 (1990).

174. CH_3ONO Predissociation by Ultrashort Laser Pulses: Population Transients and Product State Distribution, V. Engel and H. Metiu, J. Chem. Phys. 92, 2317 (1990).

175. Coherence, Transients and Interference in Photo-Dissociation with Ultra-Short Pulses, H. Metiu and V. Engel, J. Amer. Opt. Soc. B 7,1709 (1990).

178. A Theoretical Study of I_2 Vibrational Motion After Excitation With An Ultrashort Pulse, Horia Metiu and Volker Engel, J. Chem. Phys. 93, 5693 (1990).

181. Numerical Solutions of the Time-Dependent Schrödinger Equation in Spherical Coordinates by Fourier Transform Methods, C.E. Dateo, V. Engel, R. Almeida and H. Metiu, Comp. Phys. Commun. 63, 435 (1991).

188. Vibrational Coherence Effects in the Pump-Probe Studies of Photochemical Predissociation, V. Engel and H. Metiu, J. Chem. Phys. 95, 3444 (1991).

(d) Professional personnel sponsored by the grant:

Dr. S. Nagano.
Dr. Z.-P. Luo.
Dr. Volker Engel.
Dr. Robert Heather.
Dr. Raphael Almeida.
Dr. C. Dateo.

(e) Interactions:

(i) Papers presented at meetings, conferences, seminars:

1988 Seminar, Time Dependent Methods In Quantum Dynamics, Department of Chemistry, University of Colorado, February.

Invited Speaker, Time Dependent Methods for Calculating Molecule Surface Dynamics, American Physical Society Meeting, Symposium on New Computational Methods, New Orleans, LA, March.

Lecturer, Surface Molecule Collisions, International Theoretical Physics School, Institute of Theoretical Physics, Trieste, Italy, May.

Seminar, Department of Chemistry, University of Toronto, May.

Invited Speaker, Quantum Rates By Time Dependent Methods, Satellite Meeting on Chemical Reaction Dynamics, Jerusalem, Israel, August.

Invited Speaker, Thermal Rate Theory: Surface Diffusion, Gordon Conference on Atomic and Molecular Interactions, Plymouth, NH,

August 1-5.

Invited Speaker, Hydrogen Diffusion on Surfaces, Surface Science Symposium, American Chemical Society National Meeting, Los Angeles, CA, September.

Seminar, Hydrogen Diffusion, Department of Chemistry, University of Washington, November.

1989 Seminar, Electron Scattering by Adsorbed Molecules, Physics Department, University of Texas at Austin, January.

Seminar, Time Dependent Quantum Theory of Photodissociation, Department of Chemistry, University of Colorado, Boulder, February.

Seminar, Time Dependent Quantum Dynamics in Photochemistry, Department of Chemistry, University of Maryland, March.

Invited Speaker, Symposium on Solid State Dynamics, Hydrogen Diffusion on Surfaces, American Chemical Society National Meeting, Dallas, Texas, April 9-14.

Invited Speaker, International Workshop on Surface Molecule Dynamics, Copenhagen, May.

Seminar, Hydrogen Diffusion on Surfaces, DOE Pacific Northwest Laboratory, Pasco, Washington, June.

Invited Speaker, Hydrogen Diffusion on Surfaces, Conference on Quantum Monte Carlo, Los Alamos, July.

Invited Speaker, Hydrogen Diffusion of Surfaces, Gordon Research Conference on Molecule Surface Interactions, August.

Seminar, Time Dependent Quantum Theory of Photodissociation Department of Chemistry, Stanford University, November 9.

Seminar, Hydrogen Diffusion on Surfaces, Department of Chemistry, University of Houston, October.

Talk, AFOSR Contractor's Meeting, Electron Scattering by Adsorbed Molecules, Captiva Island, Florida, October.

1990 Seminar, Hydrogen Migration on Surfaces, Department of Chemistry, University of Houston, February 6.

Seminar, Hydrogen Migration on Surfaces, Department of Chemistry, Texas A & M University, February 7.

Seminar, Hydrogen Migration on Surfaces, Department of Chemistry, University of Texas, February 9.

Invited Speaker, Al-Ga Segregation of Stepped Ga As Surfaces, Gordon Conference of Chemistry of Electronic Materials, with P. Petroff, February 26-March 2.

Seminar, Hydrogen Migration on Surfaces, Department of Physics, University of California Santa Barbara, April 3.

Invited Speaker, Symposium on Classical and Quantal Simulations, ACS National Meeting, Boston, April 23-27.

Invited Speaker, Symposium on Molecular Dynamics, ACS National Meeting, Boston, April 23-27.

Seminar, Photodissociation Probed With Femtosecond Pulses, Department of Chemistry, University of California San Diego, May 22.

Invited Speaker, Quantum Theory of Hydrogen Migration on Surfaces, Fifth Workshop on Interface Phenomena, Bar Harbor, August 12-17.

Invited Speaker, Kinetic Monte Carlo Simulations of Epitaxial Growth of AlAs-GaAs Coherent Tilted Superlattices, ACS National Meeting, Washington, D.C., August 26-31.

Invited Speaker, Methods for Structure and Dynamics, Time Dependent Quantum Mechanical Studies in Complex Systems, ACS National Meeting, Washington, D.C., August 26-31.

Invited Speaker, Kinetic Processes in Epitaxial Growth, Workshop on Surface Chemistry, Irvine, Oct. 21-23.

Invited Speaker, Japan-US Workshop on Theoretical Approaches to Energy Transfer and Photochemical Processes, Honolulu, Dec. 27-30.

Invited Speaker, Workshop on Time-Dependent Phenomena in Atomic, Molecular and Optical Physics, Harvard Smithsonian Center, Cambridge, MA, Nov. 8-10.

1991 Physical Science Colloquium, Surface Diffusion and Epitaxy, IBM Research Center, Yorktown Heights, Jan 29.

Seminar, NRL Chemistry Colloquium, Diffusion on Surfaces, Jan. 31.

Seminar, Interdisciplinary Research Center on Semiconductor Materials, Imperial College, London, Simulations of AlGaAs and Si Epitaxy, March.

Seminar, Chemistry Department, University of Cambridge, Surface Diffusion, March.

Invited Speaker, Faraday Discussion on Structure and Dynamics of the Transition State, March 25-27, Nottingham, England.

Invited Speaker, Surface Migration and Epitaxy, Kendall Symposium, American Chemical Society, National Meeting, Atlanta, GA, March.

Invited Speaker, Simulations of Epitaxial Growth, Symposium on Dynamical Processes in Condensed Molecular Systems, April 29-30,

Neve-Ilan, Israel.
Seminar, Simulations of Epitaxial Growth, Department of Chemistry, Hebrew University, Jerusalem, Israel, April.
Seminar, Simulations of Epitaxial Growth, Weitzmann Institute, Rehovoth, Israel, April.
Seminar, Chemistry Department, Spectroscopy and Photochemistry on a Short Time Scale, Ben Gurion University, Beersheva, Israel, April.
Seminar, Coherence and Interference in Short Pulse Excitation of Dissociating Molecules, Institute for Theoretical Physics, Santa Barbara, CA, September 10.
Invited Talk, Simulations of Epitaxial Growth, AFOSR Meeting, Irvine, CA, October.

(ii) No consultative or advisory functions.

(f) No new inventions of patent disclosures or specific applications.